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Design of a novel Pd three-way catalyst: integration of catalytic functions in three dimensions

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Abstract

Performance of Pd catalysts for three-way conversion of HC/CO/NO is characterized using simulated auto exhaust gas over a wide temperature range from 423 to 823 K. For Pd catalysts, HC/CO/NO conversions increase sharply around 570 K. Introduction of ceria in Pd catalysts reduces NO conversion at low temperature around 600 K, while increases NO conversion at high temperature around 770 K. The lower NO conversion is attributed to a lower Pd function resulted by intimate Pd–Ce interaction. The enhanced NO conversion at high temperature is related to a higher oxygen storage capacity provided by ceria. In addition, base metal oxide additives are found to enhance Pd catalysts performance over the wide temperature range tested. An integrated Pd only catalyst washcoat architecture, consisting of a Pd top layer and a Pd–Ce bottom layer, is designed to maximize HC/CO/NO performance over a wide operating temperature range. Engine and vehicle evaluation results show that this Pd catalyst, integrating Pd sites and oxygen storage components in three dimensions, is superior in three-way performance to current Pt/Rh catalysts, and can be applied to meet stringent Californian low emission vehicle standards.

Keywords: Pd three-way catalyst; Pd–Ce interaction; Pd–base metal additive interaction

1. Introduction

Automotive catalysts have been widely used to reduce emissions of hydrocarbon, carbon monoxide and nitrogen oxides from gasoline engine powered vehicles. Pt/Pd is used in catalysts for HC/CO oxidation, and Rh-based Pt/Rh and Pd/Rh three-way catalysts are used for simultaneous removal of HC/CO/NO [1].

Rh has been a key catalytic component in TWC catalysts, and particularly for nitrogen oxide conversion. While Pt and Pd can simultaneously catalyze CO, HC and NO reactions under typical TWC conditions, these conventional Pd or Pt catalyst technologies are not as effective as Rh-based technologies, e.g. low in conversions at the stoichiometric point and narrow in operating window. Consequently, the current usage of Rh in TWC catalysts exceeds the mine ratio.

It has been a challenge to find replacement of scarce Rh in automotive catalyst while meeting the more stringent emission standards. Pd is more abundant; however, significant improvement in NO conversion is required for TWC application. Gandhi and co-workers found that MoO_3 and WO_3 additives improved the selectivity of Pd for converting nitrogen oxides to nitrogen [2–4]. Muraki et al. observed that Pd

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catalyst performance could be enhanced with lanthanum oxide additive [5]. Bell et al. investigated effect of lanthanum oxide in the Pd–La catalyst system, and suggested that strong metal–support interaction, as originally proposed by Tauster [6], were operative in the Pd–La catalysts [7–9].

This paper discusses a highly integrated catalyst washcoat design, based on a Pd-only three-way catalyst with high TWC performance, typical of that seen in Rh-based catalysts for meeting stringent emission standards.

2. Experimental

2.1. Catalyst preparation

Mixture of catalyst powders impregnated with Pd nitrate solution and other oxide additives was ball milled to reduce particle size of catalyst powders to 90% of particles less than 10 μm in water medium. The obtained slurry is then applied to a cordierite ceramic honeycomb substrate (400 cells per square inch) and excess slurry is blown out using forced air flow. The washcoated catalyst honeycomb is then dried and calcined in air. For powder reactor studies, the slurry is dried and calcined directly to obtain powder catalysts.

2.2. Catalyst evaluation

A laboratory honeycomb reactor, as shown in Fig. 1, is used to evaluate activity of honeycomb core catalysts at temperature between 423 to 823 K in a simulated auto exhaust gas stream.

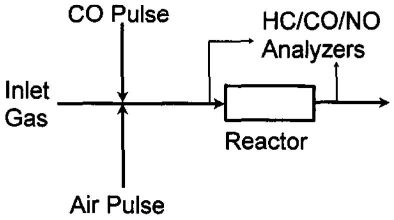

Fig. 1. Laboratory honeycomb reactor flow chart.

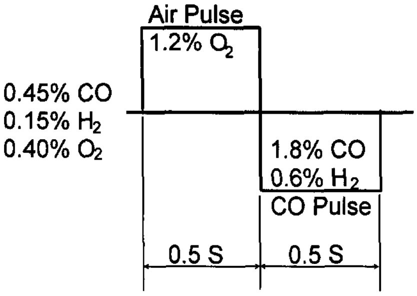

Fig. 2. Composition of simulated auto exhaust.

Catalyst core is 3.8 cm in diameter and 7.6 cm in length. Inlet gas contains 0.3% CO, 0.1% H_2, 0.35% O_2, 16.3% CO_2, 10% H_2O, 1600 ppm NO, 280 ppm C_3H_6, 280 ppm C_3H_8, 40 ppm SO_2 with the balance nitrogen. Air pulse injects air to increase O_2 concentration to 0.85% over a 0.5 s time span, and CO pulse injects CO/H_2 to 1.2% CO and 0.4% H_2 over the next 0.5 second, as shown in Fig. 2. The perturbation frequency is 1 Hz. The average gas composition for the honeycomb reactor is 0.75% CO, 0.25% H_2, 0.6% O_2, and all the other components are at the inlet gas concentration. Catalyst inlet and outlet gas compositions are determined using HC/CO/NO analyzers while raising temperature gradually from 423 to 823 K to obtain HC/CO/NO conversions at different temperatures at a space velocity of 50000 VHSV.

A laboratory micro powder reactor is used to evaluate intrinsic activity of catalyst washcoat in powder form. CO pulse is used to modulate the perturbation around the stoichiometric ratio. The average gas composition is 0.6% CO, 0.2% H_2, 0.3% O_2, 2000 ppm NO, 20 ppm SO_2 with the balance nitrogen. CO/NO conversions are measured at a space velocity of 350000 VHSV and a perturbation frequency of 0.167 Hz.

Performance of full size catalyst is evaluated using a 4.6 l vehicle according to the U.S. Federal Testing Procedure 1975.

2.3. Catalyst aging

All catalysts have been aged to simulate in-use catalyst performance before activity measurements, except that selectivity of NO reduction was measured using fresh catalysts. The laboratory honeycomb reactor aging is conducted at 1223 K for 12 h in the simulated auto exhaust gas stream. The laboratory powder reactor aging is done at 1273 K for 6 h. Full size catalysts are aged in engine exhaust gas stream on dynamometer for 75–95 h before vehicle evaluation. The maximum catalyst temperature reaches 1193 K during engine dynamometer aging.

3. Results and discussions

3.1. Proposed working mechanism of Pd catalysts

Three-way catalysts include two key catalytic ingredients: precious metal particles and cerium oxide dispersed in alumina washcoat. Precious metal particles are highly active in catalyzing HC/CO/NO conversion at stoichiometry. Auto exhaust gas composition, which is controlled by an air/fuel metering system using oxygen sensor located in the exhaust stream to feedback the air/fuel ratios, perturbates around stoichiometric ratio. Cerium oxide is mainly used to provide the so-called oxygen storage function, which store/release oxygen to assist the completion of three-way reactions. In a rich mode when exhaust gas contains more CO/HC and less O_2, ceria release oxygen for CO oxidation, and some subsequently oxidized by nitric oxide. In a lean mode when O_2 amount is significantly higher than CO/HC, ceria, which has been partially reduced during the preceding rich cycle, reacts with oxygen and nitrogen oxides to restore oxygen.

3.2. Catalyst light-off

Catalyst light-off performance is evaluated by measuring HC/CO/NO conversions while raising incoming reaction gas temperature gradually from room temperature to 823 K. Fig. 3 shows a typical light-off curve for Pd catalysts. This Pd catalyst contains Pd dispersed in an alumina washcoat, and has been aged in a simulated auto exhaust gas stream at 1223 K in the honeycomb reactor. CO/HC/NO conversions increase sharply around 560 K, as shown in Fig. 3. At 623 K, NO conversion is 66% for a 1.75 g/l Pd catalyst. After catalyst light-off, NO conversion remains nearly constant while temperature is raised gradually to 823 K. CO conversion increases sharply from 0 to 95% after light-off (570 K), and then remains constant at temperature up to 823 K. HC conversion increases to about 60% after the catalyst light-off at 570 K, and then gradually increases with increasing temperature, to 95% around 823 K.

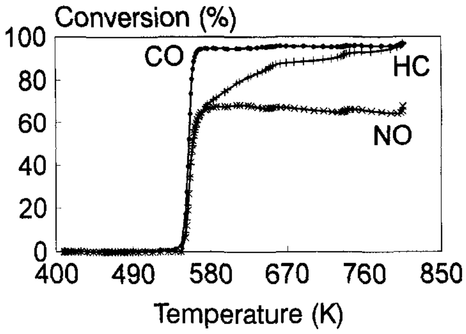

Fig. 3. HC/CO/NO light-off on Pd catalyst.

3.3. Base metal oxide additives

Effects of base metal oxide additives are summarized in Table 1. At 623 K, non-promoted Pd catalysts shows 40 and 62% NO conversion for 1.75 and 3.5 g/l Pd catalysts, respectively. Addition of base metal oxides into cata-

Table 1
NO conversions on Pd catalysts

Catalyst	Pd loading (g/l)	NO% at 620 K	NO% at 750 K
Pd	1.75	40	38
Pd	3.5	62	60
Pd + BM	1.75	66	65
Pd + BM	3.5	72	70
Pd + Ce + BM	3.5	64	84

lyst washcoat increases NO conversion to 66% on the 1.75 g/l Pd, and 72% for the 3.5 g/l Pd catalyst. It is very impressive that the 1.75 g/l Pd catalyst with base metal oxide additives gives higher NO activity than the 3.5 g/l non-promoted Pd catalyst. The high NO activity may be attributed to base metal oxides provided washcoat stabilization effect which maintain a higher catalyst surface area after high temperature aging, and promoter effects which keep Pd highly dispersed and increase the intrinsic activity of surface Pd.

3.4. Effect of ceria

When cerium oxide is incorporated into the same Pd catalyst washcoat, NO conversion increases continuously with increasing reaction temperature. As shown in Table 1, for a 3.5 g/l Pd–Ce catalyst, NO conversion increases from 64% at 623 K to 84% at 773 K. NO conversion at high temperature is significantly higher than that on the non-promoted Pd catalyst and other base metal oxide-promoted Pd catalysts. The enhanced NO activity at high temperature is attributed to the high oxygen storage function provided by the ceria added into the Pd catalyst washcoat. It should be noted that at 623 K, addition of ceria into the catalyst decreased NO conversion over the 3.5 g/l Pd–Ce catalyst to 64% from 72% for the 3.5 g/l Pd catalyst, which is slightly lower than 66% NO conversion over the 1.75 g/l base metal oxide-promoted Pd catalyst. The results indicate clearly that at low temperature, e.g. at 623 K, three-way reactions take place exclusively on Pd surface. High oxygen storage capacity would not contribute in three-way reactions probably due to the fact that oxygen mobility is too low to participate in the reaction at such low temperatures. It is also clear that interaction between Pd and ceria reduces the effectiveness of Pd metal particles in catalyzing the three-way reactions. This has also been confirmed for catalysts containing Pd and ceria where the base metal oxide additives were not used.

Table 2
XPS characterization of Pd catalysts

Reduction temperature (K)	Pd	Pd–Ce
none	0.18 Pd(+ +)	0.10 Pd(+ +)
373	0.17 Pd(0, + +)	0.08 Pd(+ +)
473	0.14 Pd(0)	0.07 Pd(0, + +)
573	0.13 Pd(0)	0.08 (0, + +)
673	0.13 Pd(0)	0.10 Pd(0, +)
773	0.13 Pd(0)	0.08 (0, +)

3.5. Pd–Ce interaction

XPS is used to characterize Pd–ceria interaction in the Pd catalysts. As shown in Table 2, Pd exists exclusively in the 2 + charged Pd oxide state. The same catalysts are then reduced in 7% hydrogen (nitrogen balance) gas flow at temperature between 373 to 773 K. For the ceria-less catalyst, Pd exists exclusively as Pd metal after reduced at 473 K, indicating that complete reduction of Pd oxide to Pd metal is achieved at temperature below 473 K. In comparison, for the ceria-promoted Pd catalyst, a significant portion of Pd still remains as 2 + charged Pd oxide state even after reduction at 573 K, and some remains in partially reduced oxide form as 1 + charged Pd after reduction at 773 K. It is clear that ceria retards reduction of Pd oxide through a Pd–Ce interaction.

3.6. Reaction path

To explain the above experimental results, a reaction path is proposed, as depicted in Fig. 4. Pd is effective at converting HC/CO/NO around stoichiometry at relatively low temperature. Oxygen from ceria contribute to the

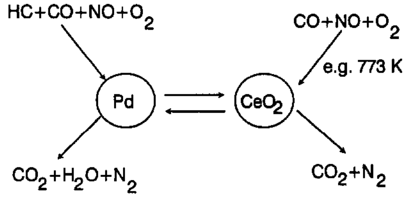

Fig. 4. Proposed reaction paths.

CO/NO reactions at relatively high temperature, e.g. 773 K. Pd and ceria interact strongly, and the activation temperature of oxygen from ceria might be modified significantly by the Pd–Ce interaction through spill-over and reverse spill-over mechanisms.

4. Catalyst design

The above experimental results indicate clearly that Pd is effective in catalyzing steady state TWC reactions at low temperature. At high temperature, intimate Pd–Ce interaction reduces Pd effectiveness, however, it provides a high oxygen storage capacity to enhance TWC activity under perturbation conditions. In order to synthesize a high performance Pd catalyst, Pd–Ce interaction needs to be optimized to maintain both a high Pd effectiveness and a high oxygen storage capacity. Aimed at maximizing catalyst performance, Pd and ceria functions are integrated in three dimensions in the Pd catalyst washcoat, as shown in Fig. 5. The first layer on the top of honeycomb substrate contains Pd and ceria; the second layer, which is on the top of the first layer, contains Pd dispersed in an alumina washcoat. Both Pd catalyst layers are incorporated with base metal oxide stabilizers. Pd in the top layer is physically separated from ceria to avoid detrimental Pd–Ce interaction, and a high Pd effectiveness is achieved by using base metal oxide promoters as previously described. In the bottom layer, Pd is purposely associated with ceria to utilize intimate Pd–Ce interaction in facilitating oxygen migration from ceria to participate in the CO/NO reactions. The Pd catalyst layer provides high Pd activities at low temperatures. The Pd–Ce layer offers a high oxygen storage capacity which thus gives a high three way activity at high temperature. Consequently, the designed Pd catalyst has a high performance optimized for the whole operating temperature range. In addition, this three dimensional integrated structure enables selective NO reduction in the top layer where maximum CO concentration is provided for the NO reduction, and the integration of the two distinct catalyst layers gives further enhanced three-way performances.

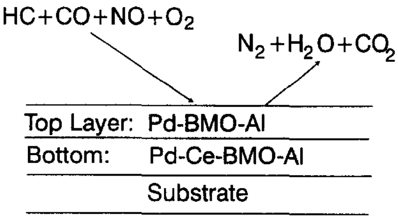

Fig. 5. Architecture of the Pd catalyst.

Table 3
Performance characterization of Pd catalysts

Catalyst	CO (% at 623 K)	NO (% at 623 K)	CO (% at 823 K)	NO (% at 823 K)
Pd–Ce	60	31	68	47
Pd	69	53	62	33
Pd/Pd–Ce	65	45	74	51

5. Performance characterization

5.1. Micro powder reactor

In order to confirm the novelty of the architecture of the designed Pd catalyst, a micro powder reactor is used to compare performance of the Pd, the Pd–Ce catalysts and their integration. As shown in Table 3, the Pd–Ce catalyst provides CO/NO conversions higher than the Pd catalyst at high temperature, and the Pd catalyst shows higher activities at low temperature. These are in good agreement with those previously discussed results obtained on the honeycomb reactor. Integrating the two distinct Pd and Pd–Ce catalysts into one formulation, the Pd//Pd–Ce catalyst gives CO/NO activity in between the Pd and the Pd–Ce catalysts at low temperature. This correlates the activities of Pd species in the Pd and the Pd–Ce catalysts almost linearly, further supporting the above discussion that CO/NO reactions take place

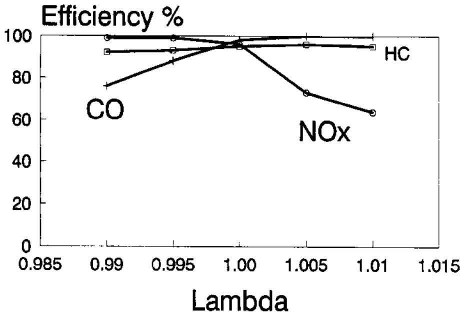

Fig. 6. HC/CO/NO conversions of the designed Pd catalyst.

exclusively on Pd surface at low temperature. However, the Pd//Pd–Ce catalyst provides CO/NO activity much higher than either the Pd or the Pd–Ce catalysts at high temperature. This indicates clearly that a desired synergism between the Pd and the Pd–Ce catalysts is obtained in the Pd//Pd–Ce catalyst system. This synergism arises probably from the optimized integration of a high Pd effectiveness and a high oxygen storage capacity. In conclusion, the novelty of the designed Pd catalyst structure is confirmed based on intrinsic activities of the Pd catalysts and synergism between them.

5.2. Engine sweep test

The designed Pd catalyst (3.5 g/l Pd) was evaluated in an engine exhaust stream in comparison with an advanced Pt/Rh catalyst (1.75 g/l, Pt/Rh = 5/1). As shown in Figs. 6 and 7, HC/CO/NO conversions are measured at 723 K, 64000 VHSV, a frequency of 1 Hz and an perturbation amplitude of ±0.03. Lambda is defined as the ratio of exhaust air/fuel ratio and the theoretical air/fuel ratio for complete fuel combustion (14.6 air to 1 fuel). It is clear that both the designed Pd catalyst and the advanced Pt/Rh catalyst show high HC/CO/NO conversions and wide operating windows. In conclusion, for the Pd catalyst, high TWC performance typical of that seen in Rh-based catalyst has been obtained, such as a wide operating window and high three-way conversions at the stoichiometric point.

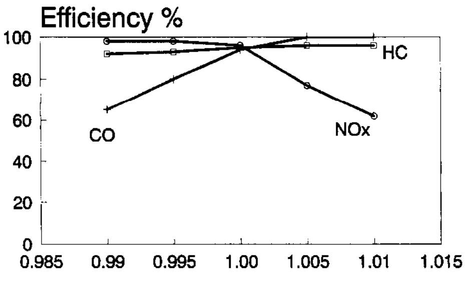

Fig. 7. HC/CO/NO conversions of Pt/Rh catalyst.

5.3. Selectivity of NO reduction

Rh-based catalysts are known to have high selectivities for NO reduction to nitrogen. Several reports indicated that Pd catalysts might produce more ammonia as the product of NO reduction. The designed Pd catalyst (3.5 g/l Pd) is compared to the advanced Pt/Rh catalyst (1.41 g/l) for ammonia formation. In this case, neither catalyst was aged. In Fig. 8, the ammonia formation is shown as a function of lambda

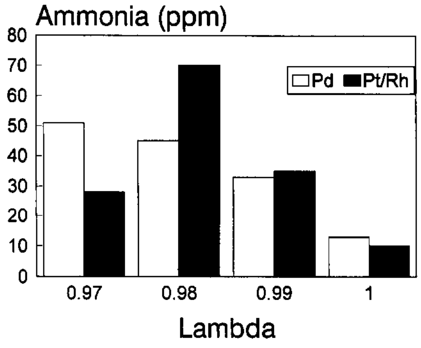

Fig. 8. Comparison of ammonia formation on Pd and Pt/Rh catalysts.

Table 4
HC/CO/NO conversions in vehicle FTP evaluation

Catalysts	HC (%)	CO (%)	NO (%)
Pd	95.1	84.4	84.1
Pt/Rh	89.8	80.5	81.9

at 748 K, ±0.5 A/F, 1.0 Hz and 80 000 VHSV. While the Pd catalyst tends to make slightly more ammonia than the Pt/Rh catalyst under very rich A/F conditions, the reverse is true under stoichiometric operating conditions. In conclusion, the designed Pd catalyst and the Pt/Rh catalysts are comparably selective for NO reduction to nitrogen for most vehicle applications.

5.4. Vehicle evaluation

A 0.69 l brick of the designed Pd catalyst (3.5 g/l Pd) and a brick of the advanced Pt/Rh catalyst (1.75 g/l) are installed in an identical location in exhaust system of a 4.6 l vehicle, respectively. Both catalysts have been aged in an engine exhaust stream for 75 h. The maximum catalyst temperature was 1200 K. Vehicle testing was done according to the federal testing procedure. As shown in Table 4, total FTP HC/CO/NO conversions are 95.1%, 84.4% and 84.1% for the Pd catalyst, and 89.8%, 80.5% and 81.9% for the Pt/Rh catalyst, respectively. It should be noted that the Pd catalyst is superior in HC conversion and equal in NO conversion to the Pt/Rh catalyst. The data confirm that equal or higher TWC performance is achieved on the designed Pd catalyst in comparison with the advanced Pt/Rh catalyst.

6. Summary

Catalyst design is practised in developing a commercial Pd three-way catalyst technology. Three key parameters are identified for Pd catalysts: 1, base metal oxide additives enhance Pd catalyst performance; 2, Pd–Ce interaction reduces Pd effectiveness; 3, intimate Pd–Ce contact provides a high oxygen storage capacity. An architecture of a novel Pd catalyst washcoat, integrating Pd, Ce and base metal oxide additives in three dimensions, is designed to maximize catalyst performance. The designed Pd catalyst shows three-way performance superior to advanced Pt/Rh catalysts [10].

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